

# Growth and Characterization of a New Inorganic NLO Crystal for Efficient Second Harmonic Generation (SHG)

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**Abstract:** *Materials with large nonlinear optical susceptibilities are of current interest in the area of harmonic generation and optical modulation. Materials showing high optical non linearity have potential applications in signal transmission, data storage, optical switching, laser printing, displays, inflorescence, photolithography, remote sensing, chemical and biological species detection, high resolution spectroscopy, medical diagnosis and underwater monitoring & communication. In recent few years, several novel NLO crystals have been developed for efficient second-harmonic generation (SHG) and other parametric processes. In the inorganic family crystals, borate crystals have attracted much attention due to their instinctive properties. Such a new inorganic nonlinear optical single crystal of Magnesium Cadmium Borate (MCB) has been successfully grown from aqueous solution using the slow evaporation technique at room temperature. The crystals obtained using the aforementioned method were characterized using different techniques. The crystalline nature of the as-grown crystal of MCB was analyzed using powder X-ray diffraction. The optical transmission study of the MCB crystal revealed high transmittance in the entire UV-VIS region, and the lower cut-off wavelength was determined to be 230 nm. The presence of functional groups has been estimated qualitatively from the Fourier transform infrared spectroscopy. The frequency doubling property of NLO crystal was verified through second harmonic generation (SHG) studies.*

**Keywords:** Nonlinear optical material, powder X-ray diffraction analysis, UV optical studies, second harmonic generation

## I. INTRODUCTION

### 1.1 CRYSTAL GROWTH

Crystal growth is a major stage of a crystallization process, and consists of the addition of new atoms, ions, or polymer strings into the characteristic arrangement of the crystalline lattice. The process of crystal growth includes nucleation, growth and coarsening. For a new phase to grow, a stable embryo of the new phase must form first. This process is called nucleation. The nucleus serves as a template for the crystal to grow. The growth of the crystal involves interface reaction and mass/heat transfer. In the search for new electronic materials, crystal growth plays an essential part, while crystal growth theory provides an ideal testing ground for the interplay of atomic (microscopic) and classical (macroscopic) concepts and the most practical experimental realities.

### 1.2 CRYSTAL GROWTH TECHNIQUES

Crystal growth may be a difficult task and therefore the technique followed for crystal growth depends upon the characteristics of the materials under investigation, like its temperature, Volatile nature, solubility in water or different organic solvents and then on the fundamental growth ways on the market for crystal growth area unit loosely.

- Growth from melt.
- Growth from vapor.
- Growth from solution.
- Growth from solid.

The fundamental common principle altogether these ways is that a nucleus is initial shaped and it grows into one crystal by organizing and collection ions or molecules with specific interactions and bonding, so the method is slow and multiple nucleation is decreased.

### **1.3 ADVANTAGE AND DISADVANTAGE OF SOLUTION CRYSTAL GROWTH**

#### **1.3.1 Advantage**

- Growth from free surface
- Growth of large oriented single crystal
- Control of atmosphere

#### **1.3.2 Disadvantage**

- High vapor pressure materials
- Liquid phase encapsulation
- No reproductivity of the crystal shape

### **1.4 Single crystal growth**

The absence of the defects associated with grain boundaries can give single crystals unique properties, particularly mechanical, optical and electrical. These properties, in addition to making them precious in some gems, are industrially used in technological applications, especially in optics and electronics.

A single crystal is a material in which the crystal lattice of the entire sample is continuous and unbroken to the edges of the sample, with no grain boundaries. The absence of the defects associated with grain boundaries can give single crystals unique properties, particularly mechanical, optical and electrical. These properties, in addition to making them precious in some gems, are industrially used in technological applications, especially in optics and electronics.

### **1.5 NON LINEAR OPTICS**

Non-linear optics (NLO) is an innovative area of research and development which plays a key role in the field of optoelectronics and photonics.[1] Materials with large second order optical non-linearities find wide applications in the area of laser technology, laser communication and data storage technology.[2] In recent years, several studies dealing with organic, inorganic and semi-organic molecules and materials for non-linear optics are being published due to the increasing demand for processable materials in the photonics applications.[1],[6] The non-linear optical responses induced in various molecules in solution and solids are of great interest in many fields of research.

The interaction of the electromagnetic field of light (normally high intensity laser light) with a nonlinear optical (NLO) material can result in the generation of new electromagnetic fields. As light passes through a species, its electric field interacts with inherent charges in the material causing the original beam to be altered in phase, frequency, amplitude and polarization. Basically, all materials exhibit optical phenomena. This includes all forms of matter (i.e) gases, liquids, and solids. The power of the optical fields require to observe these effects varies over many orders of magnitude, depending on the detailed nature of the electronic structure of the atomic and molecular constituents of the medium, their dynamical behavior, as well as the symmetry and details of their geometrical arrangement in the medium. The important nonlinear optical materials from the device point of view are generally in solid formats and must meet a wide variety of ancillary material requirements for optical use. In general, they will require extraordinary stability with respect to ambient conditions and in high intensity light sources.

Some materials change light passing through them, depending upon orientation, temperature, light wavelength etc. (red light, lower wavelength) releasing one photon of accumulated higher energy (blue and green light, higher wavelength). NLO materials typically have a distinct crystal structure, which is anisotropic with respect to electromagnetic radiation.

The importance of nonlinear optics is to understand the nonlinear behavior in the induced polarization and to analyze and to control its impact on the propagation of light in the matter.

### **1.5.1 ORGANIC NLO CRYSTAL**

The organic non-linear materials show the non-linear behavior of light due to presence of conjugated  $\pi$ - $\pi$  \* electrons. All these crystals have a good dynamic structure and transparent in nature. These are second order frequency generator organic non-linear materials. The materials are non-centrosymmetric in nature and applicable in optical modulators, optical devices, laser frequency modulators. UV- Spectroscopy shows transparent nature in the entire visible region and near infrared region. On the contrary, precise processing technologies for organic crystals have hardly been developed. Since organic materials are very brittle, having hygroscopic properties, low melting temperatures and particular cleavage planes owing to weak intermolecular bonding, conventional processing technologies used for inorganic materials cannot be extrapolated to obtain arbitrary shape crystals and fine optical surfaces. A disadvantage of organic nonlinear optical (NLO) materials is often their low physico-chemical stability.

### **1.5.2 INORGANIC NLO CRYSTAL**

New inorganic nonlinear-optical (NLO) materials are necessary for solid- state lasers to generate coherent radiation in the ultraviolet (UV) and deep-UV regions. Inorganic materials are defined as chemical compounds that contain no carbon (C). However, elementary carbon (C) (as graphite or diamond) and compounds of carbon and, for example, nitrogen, oxygen, or silicon are also classified as inorganic. Examples of such inorganic compounds include carbon monoxide (CO), silicon carbide (SiC), and carbonic acid (H<sub>2</sub>CO<sub>3</sub>), and salts thereof. All other types of carbon-containing compounds are called organic materials. Inorganic materials, exhibiting second order nonlinear optical properties have attracted in the recent past due to their ability to process into crystals, wide optical transparency domain, large nonlinear figure of merit for frequency conversion, fast optical response time and wide phase matchable angle. Molecular hyperpolarizability of inorganic nonlinear optical crystal are used in optical switching (modulation), frequency conversion (SHG, wave mixing) and electro- optic applications especially in EO modulation. Historically, inorganic NLO materials have been chronicled more extensively inorganic oxide crystal, LiNbO<sub>3</sub>, KNbO<sub>3</sub>, KDP and KTP, etc., have been studied for device application like piezoelectric, ferroelectric and Electro-optics.

### **1.5.3 SEMI ORGANIC NLO MATERIAL**

In semi organic materials, the organic ligand is ionically bonded with inorganic host that resulted in new materials having high optical nonlinearities. Complexes of amino acids with inorganic salts are promising materials for optical applications such as optical communication, optical computing, optical information processing, optical disk data storage, laser fusion reaction, laser remote sensing. The high nonlinearity, high resistance to laser-induced damage, low angular sensitivity and good mechanical hardness of semi-organic crystals combine in the strong NLO properties and chemical flexibility of organic materials with the physical sturdiness and excellent transmittance of inorganic materials

## **II. EXPERIMENTAL**

### **2.1 MATERIAL SELECTION**

As compared to organic crystals, the inorganic crystals have good physio- chemical stabilities, short UV cut-off wavelength and large second order non- linearities. Due to these reasons, the inorganic crystals are gaining popularity in the field of nonlinear optics. Most recent work has demonstrated that organic crystals can have very large non-linear susceptibilities as compared with inorganic crystals, but their use is impeded by low optical transparencies, poor mechanical properties, low laser damage thresholds and inability to produce and process large crystals. The inorganic materials are widely used in these applications because of their high melting point, high mechanical strength and high degree of chemical inertness. In the inorganic family crystals, borate crystals have attracted much attention due to their instinctive properties. The first borate based NLO crystals KB<sub>5</sub>O<sub>8</sub>.4H<sub>2</sub>O (KB<sub>5</sub>) – (1975). Intense work began after the advent of LBO and BBO crystals. (Examples lithium borate LiB<sub>3</sub>O<sub>5</sub> (LBO),  $\beta$ -Ba<sub>2</sub>B<sub>2</sub>O<sub>4</sub> (BBO), CsLiB<sub>5</sub>O<sub>10</sub>(CLBO), SrBe<sub>2</sub>B<sub>2</sub>O<sub>7</sub>(SBBO), etc.). Have excellent transmission properties in combination with NLO behaviour. Therefore,

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these new materials used for NLO applications and expanding the frequency range provided by the conventional laser sources. In the present work, a novel inorganic NLO material, Magnesium Cadmium Borate (MCB) is grown, and its optical properties are investigated.

## 2.2 EXPERIMENTAL PROCEDURE

### 2.2.1 Synthesis

The Magnesium Cadmium Borate (MCB) single Crystal was synthesized by magnesium nitrate, Cadmium nitrate and boric acid in amount of 8.2305 g/mol, 10.1758 g/mol and 3.425 g/mol in double distilled water. The purity of the synthesized salt was further increased by repeated recrystallization. The crystal synthesise shown in the figure 2.1.

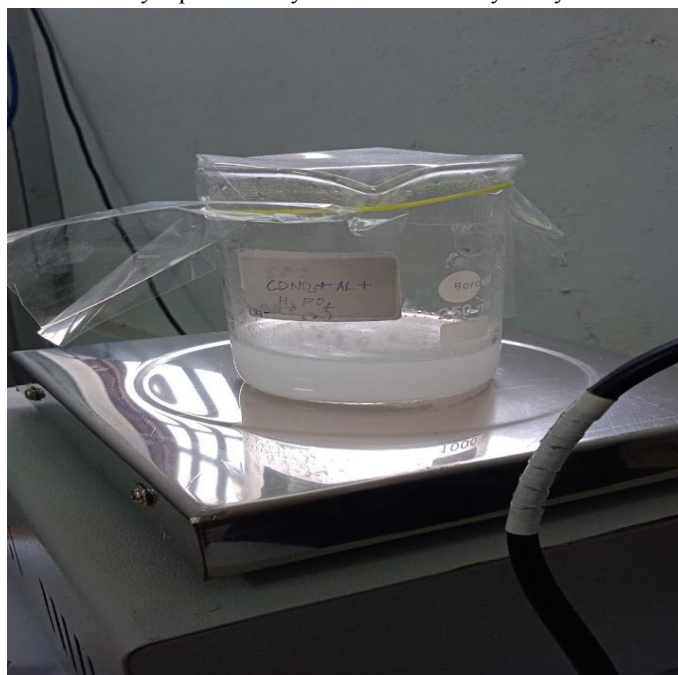
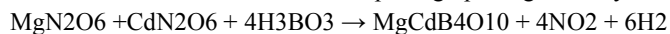


FIG 2. 1 CRYSTAL SYNTHESIZE

### 2.2.2 Crystal growth

Magnesium Cadmium Borate (MCB) was synthesised by slow evaporation technique. The starting materials used for synthesis were of analytical reagent grade of Magnesium nitrate, Cadmium nitrate and boric acid at 1:1:1 ratio. The calculated amount of Magnesium nitrate, Cadmium nitrate and boric acid salts were added with double distilled water according to the solubility and, finally the whole solution was mixed with continuous stirring for 1 hours using magnetic stirrer to obtain homogenous mixture. The completely dissolved solution was filtered using whatman filter paper to remove the suspended impurities and allowed to crystallize by slow evaporation method at room temperature for two months of the time period. Once seed crystals are obtained recrystallization is done by filtering the solution and one seed crystal is dropped in that solution and again kept for evaporation. Finally a well-defined Magnesium Cadmium Borate Crystal with dimensions 8x8x4 mm<sup>3</sup> was obtained. The photograph of grown crystal is shown in the Fig.2.2



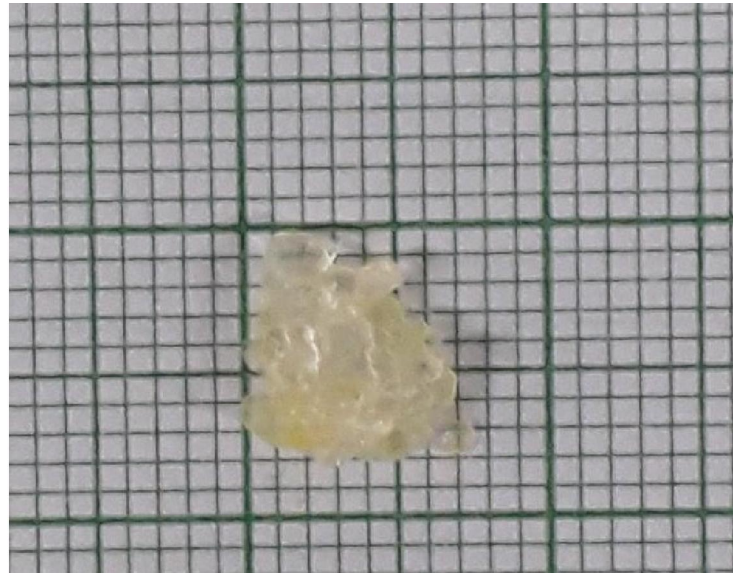


FIG 2.2 Grown crystal

### III. RESULTS AND DISCUSSION

#### 3.1 Powder X-ray diffraction analysis

Powder XRD for grown Magnesium Cadmium Borate (MCB) crystals was conducted, and the XRD pattern is shown in Figure 3.1. The powder sample was scanned over the range of 10–80° at a scan rate of 0.2°/s using CuK $\alpha$  radiation with a wavelength of 1.545Å. The obtained powder X-ray diffraction data were analyzed and compared with JCPDS data. The strong orientation is reflected by the peak at 27.97°, 28.25°, 28.39°, 29.13° confined the presence of magnesium nitrate and Cadmium nitrate. Peaks at 58.16° and 58.34° show the presence of boric acid. The limited number of sharp peaks without any broadening in the XRD pattern confirms that the as-grown MCB possesses good crystallinity.

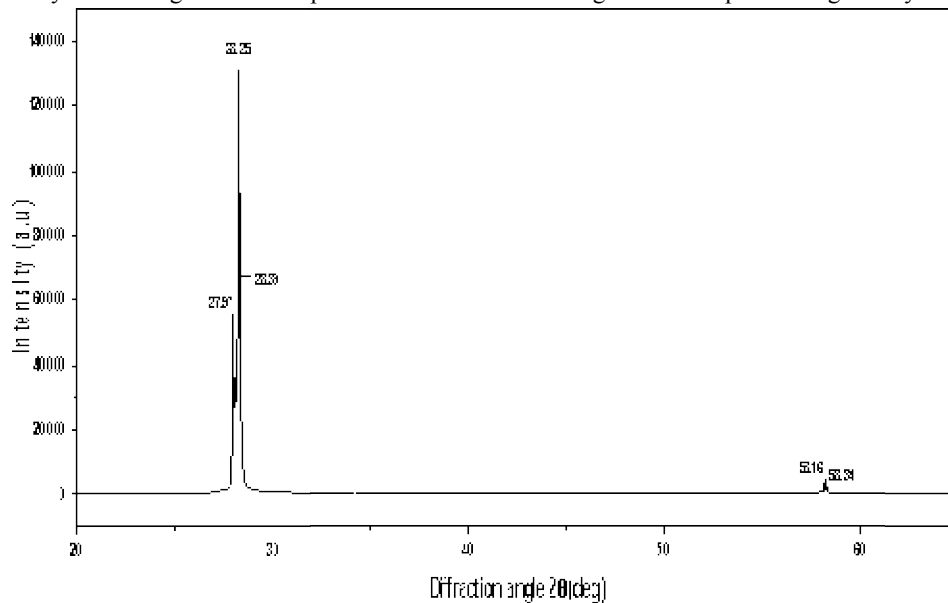


FIG 3. 1 Powder X-ray diffraction pattern for MCB crystal

### 3.2 Fourier transform infrared spectral analysis (FTIR)

Infrared spectrum studies were carried out to expound the presence of functional groups. In the FT-IR spectrum of grown crystal of MCB, the peaks are observed according to the wave number ranging from 4000 - 400 cm<sup>-1</sup>. The sample is made as a pellet by using KBr. The FTIR spectrum of Magnesium Cadmium Borate crystal (MCB) is shown in Figure 3.2. The spectrum shows the presence of all the functional groups in MCB crystal. The N-H stretch and O-H stretching are observed at 3225.39 cm<sup>-1</sup> and 2514.71 cm<sup>-1</sup>. The Nitrogen atoms presence show N-O anti symmetric stretching that are observed at 1543.31 cm<sup>-1</sup> as strong absorption. The medium B-O Asymmetric stretching is observed at 1454.60 cm<sup>-1</sup> and 1387.57 cm<sup>-1</sup>. The O=C=O stretching shows the strong absorption at 2383.16 cm<sup>-1</sup> and 2339.18 cm<sup>-1</sup>. The C-O stretching with strong absorption observed at 1193.29 cm<sup>-1</sup>. C=C bending was observed at 887.92cm<sup>-1</sup> and 810.34cm<sup>-1</sup>. Peaks at 643.9 cm<sup>-1</sup> shows B-O symmetric stretching. The N-H stretch, O-H stretch, N-O stretch and B-O stretch confirms the presence of nitrate and acid groups in grown crystal. Table 1. shows the assigned functional groups.

Table 1. FTIR assignment for MCB compound

FTIR EXPERIMENTAL VALUES	Assignments
3225	N-H STRETCH
2514	O-H STRETCH
1543	N-O STRETCH
2383	O=C=O STRETCHING
1454	B-O ASYMMETRIC STRETCH
643	B-O SYMMETRIC STRETCH
887,810	C=C BENDING

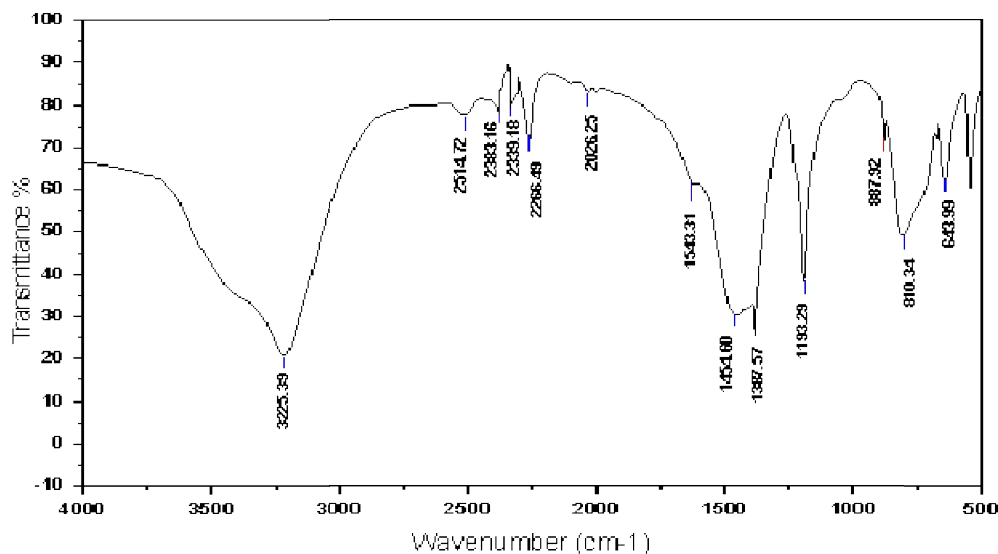


Figure 3.2 FTIR spectrum of MCB

### 3.3 UV-Visible spectral analysis

Since single crystal is mainly used in optical applications, the optical transmissions range and the frequency of cut off wavelength (200-400nm) are essential for the SHG output in the range for using lasers applications. The optical absorption plays an important role in identifying the potential of the NLO material.

The optical absorption spectra of Magnesium Cadmium Borate crystal was recorded in the region between 200nm-800nm, at a scanning speed of 200nm/min using JASCO UV-Vis NIR spectrometer. The recorded spectra shown in Figure 3.3. The absorbance found to be good in the entire visible and IR region. The spectrum shows two peaks, one at 266 nm corresponds to  $\pi$ - $\pi^*$  transition and another intense peak at 230nm corresponds to  $n$ - $\pi^*$  transition. The cut-off wavelength of MCB crystal has good absorbance at 230nm. So MCB single crystal found to be suitable for optoelectronic applications.

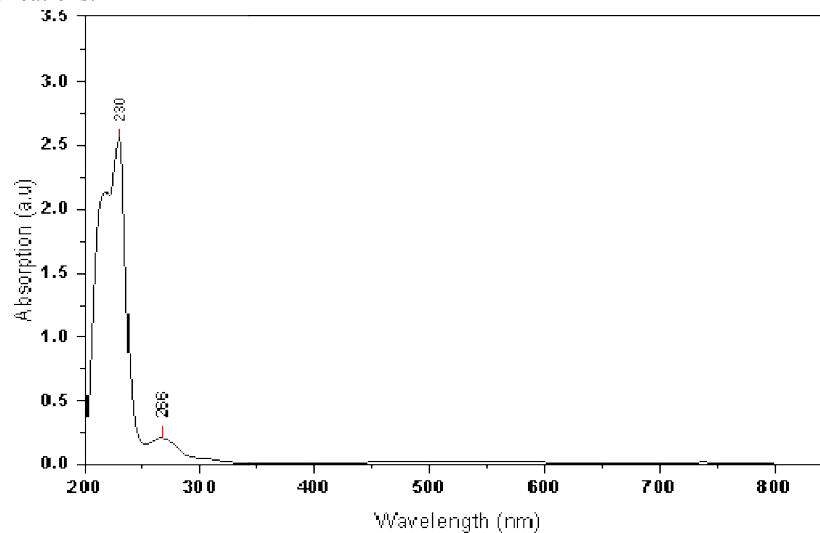


Figure 3.3. Absorption spectrum of MCB crystal

### 3.4 Optical Band gap Energy

For optical device fabrication, the crystal should have high transparency in a considerable range of wavelength. The UV cut-off wavelength of the grown MCB crystal was found to be 230nm and it is useful to make them potential material for optical device fabrication. The optical absorption coefficient ( $\alpha$ ) was calculated using Beer's law. The band gap energy ( $E_g$ ) was calculated from linear part of the Tauc's plot drawn between  $(\alpha h\nu)^2$  and photon energy ( $h\nu$ ). The band gap energy of the grown crystal MCB was plotted in the Figure 3.4. The band gap of the MCB crystal is found to 5.25eV.

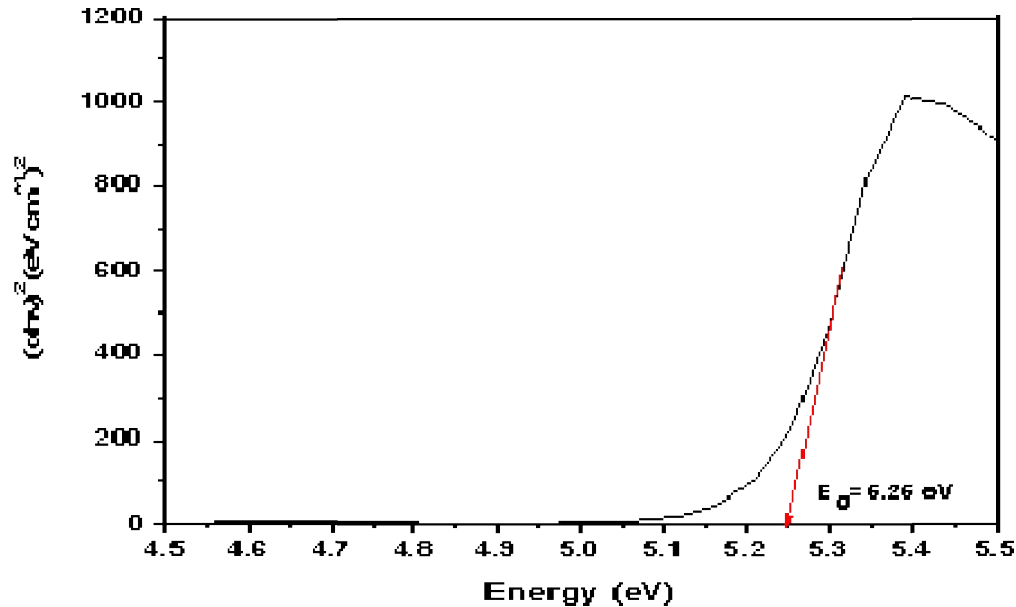


FIG 3.4 Band gap energy of the MCB crystal

### 3.5 Kurtz and perry SHG test

Non-centrosymmetric crystals need to possess NLO efficiency which has been tested using Kurtz powder technique. When the output frequency is doubled in the grown powdered sample after passing a beam 1064nm from Q-switched Nd: YAG laser the NLO efficiency is tested. The MCB crystal emits bright green light ( $\lambda=532$  nm) proving that it possesses NLO efficiency. The SHG efficiency of MCB crystal is 1.36 times greater than KDP crystal. This result recommends that the Magnesium Cadmium Borate crystal can be efficient for nonlinearity optical device application.

### 3.6 Thermogravimetric analysis

The TGA and DTA curves of Magnesium Cadmium Borate (MCB) are shown in Figs 3.5. The TGA measures weight change of a sample over a temperature range. DTA measures heat differences between a reference sample and a sample of interest over a temperature range. To find out the melting point and any kind of phase transition of Magnesium Cadmium Borate (MCB), the DTA and TGA analysis are performed with the help of an instrument SDTQ 600 V8.3. The sample was heated at a rate of 50°C/min in protected nitrogen gas flow. It is observed that the material undergoes an irreversible endothermic transition at about 128.51°C where the decomposition starts between 128.51°C and 180.12°C. It indicates that the crystal is stable up to 180.12°C. Magnesium Cadmium Borate (MCB) is fully decomposed up to 800°C. The good degrees of crystallinity of the grown crystals are shown by the sharpness of the endothermic peak. It can also be seen on the TGA curve that the weight loss starts at 128.51°C and ends at 800°C. The DTA curve shows an endothermic peak around 301.51°C which indicates the weight loss due to the liberation of a volatile substance. From the TGA curve, a sharp slope up to 180.12°C corresponds to the removal of almost all the compound as a gaseous product. The TGA and DTA analysis does not show any kind of phase transition.

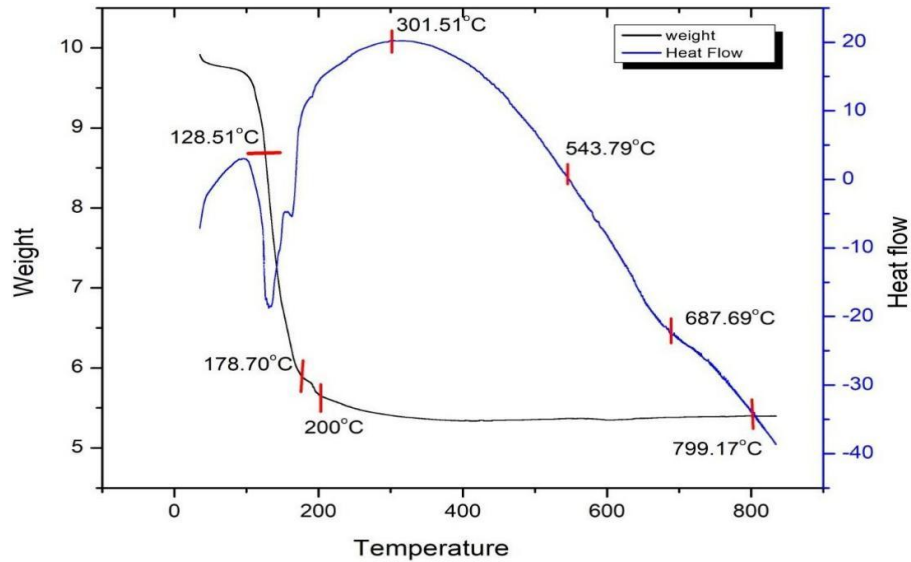


FIG 3.5 The TGA and DTA curves of Magnesium Cadmium Borate

**3.7 Crystal surface analysis by SEM**

The surface morphology of Magnesium Cadmium Borate crystals were analysed by scanning electron microscope (SEM) which is used to extract the information about size and shape of the particles present in the crystal. The surface morphology of the Magnesium Cadmium Borate crystal is shown in Fig.3.6 and the following observations have been made from SEM images.

- (i) At a magnifications of 20kv and at a scale of 20 μm, the crystals have smoothed surfaces. The significant differences can be observed from the following magnification and scales.
- (ii) At a magnifications of 20kv and at a scale of 50 μm
- (iii) At a magnifications of 20kv and at a scale of 20 μm
- (iv) At a magnifications of 20kv and at a scale of 5 μm

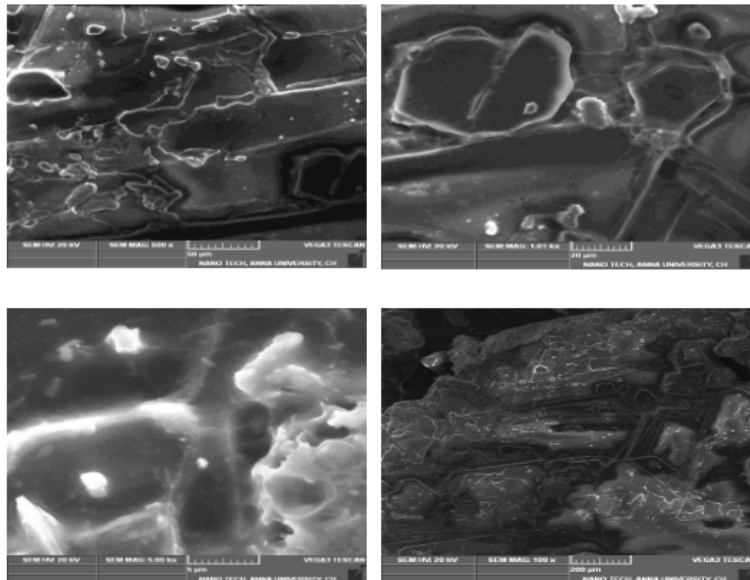


FIG 3.6 The surface morphology of Magnesium Cadmium Borate crystals

#### IV. CONCLUSION

The design, discovery and growth of novel materials, especially in single crystal form, represent national core competency that is essential for scientific progress and long-term economic growth. New materials lay at the core of many new and existing technologies, such as semiconductor electronics, solid state lasers, radiation detectors, compact disk storage, both cellular and optical communications, solar cells, fuel cells and catalysts. Single crystals are often required to achieve a materials' full functionality as well as to completely elucidate its properties. The effective NLO single crystals with efficient optical frequency conversion are the key elements for the development of laser systems, telecommunication, optical information processing, high optical disk data storage, wide range tunable sources of coherent illumination in ultra-violet, visible and infrared spectral ranges. Hence, there is a great demand to synthesize new NLO materials and grow their single crystals.

A new inorganic Magnesium Cadmium Borate (MCB) compound was synthesized using Magnesium nitrate, Cadmium nitrate and Boric acid taken in equal ratio and the crystals were grown by slow evaporation technique at room temperature of 30°C.

Powder X-ray diffraction analysis confirmed the crystalline nature of the grown crystal. The FTIR spectrum recorded for the grown sample confirms the presence of acid and nitro functional groups in the grown crystal. The optical study revealed the good transparency of the grown crystal in wide wavelength range with the lower cut-off wavelength 230nm which suits the crystal for various electro optic applications. The SHG measurement shows that the grown Magnesium Cadmium Borate crystal has higher efficiency than KDP crystal. In view of the good optical properties, better SHG efficiency of MCB crystal would be a suitable material for nonlinear optical device applications.

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